

Atty. Docket No. IDR0020
Application No: 10/789,317

Remarks

Applicant and his representatives wish to thank Examiner Johnson for the thorough examination of the present application, the detailed explanations in the Office Action dated March 18, 2008 and especially for the very helpful and courteous in-person interview on April 23, 2008. The following remarks shall summarize and further expand upon the topics and issues discussed.

Claims 1, 4, 7-12, 26, 29 and 33 have been amended. Claim 6 has been cancelled, and the limitations thereof have been combined with Claim 1. Claims 39-73 have been cancelled. New Claims 74-111 have been added. No new matter is introduced by the present Amendment.

The present invention relates to a method of making a hydrogenated Group IVA compound. The method, as recited in Claim 1, comprises the steps of:

- a) reacting one or more reducible Group IVA compound(s) with a metal hydride to form a metal-contaminated, hydrogenated Group IVA compound, said metal-contaminated, hydrogenated Group IVA compound consisting essentially of (i) Si and/or Ge, and (ii) hydrogen; and
- b) washing said metal-contaminated, hydrogenated Group IVA compound with a washing composition comprising deionized water to decontaminate said metal-contaminated, hydrogenated Group IVA compound.

The method recited in Claim 74 comprises the steps of:

- a) reacting one or more reducible Group IVA compound(s) with a metal hydride to form a metal-contaminated, hydrogenated Group IVA compound, said metal-contaminated, hydrogenated Group IVA compound consisting essentially of i) Si and/or Ge, and ii) hydrogen;

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- b) washing said metal-contaminated, hydrogenated Group IVA compound with a washing composition comprising an immiscible polar solvent to decontaminate said metal-contaminated, hydrogenated Group IVA compound; and
- c) separating said washing composition containing metal contaminants from said hydrogenated Group IVA compound.

The cited reference (Matsuki et al., U.S. Pat. No. 6,503,570; hereinafter, "Matsuki") neither discloses nor suggests washing a metal-contaminated, hydrogenated Group IVA compound with a washing composition comprising deionized water to decontaminate the metal-contaminated, hydrogenated Group IVA compound (Claim 1, step (b)), nor does Matsuki disclose or suggest washing a metal-contaminated, hydrogenated Group IVA compound with a washing composition comprising a polar immiscible solvent, and separating the washing composition containing metal contaminants from the hydrogenated Group IVA compound (Claim 74, steps (b)-(c)). Thus, Claims 1 and 74, and all claims dependent directly or indirectly therefrom, are patentable over Matsuki.

The Rejection of Claims 1, 3-16, 18-28, 37 and 38 under 35 U.S.C § 102(b)

The rejection of Claims 1, 3-16, 18-28, 37, and 38 under 35 U.S.C. § 102(b) as being anticipated by Matsuki is respectfully traversed.

Matsuki discloses two methods of preparing silylcyclopentasilane. In the first embodiment, diphenyldichlorosilane is subjected to lithium-mediated cyclization in dry, argon purged tetrahydrofuran (THF) (cf. Matsuki, col. 8, ll. 60-67). The reaction mixture is poured into ice water to precipitate the reaction product (cf. Matsuki, col. 9, ll. 1-2). The mixture is subsequently filtered, and the retained precipitate washed sequentially with water and cyclohexane (cf. Matsuki, col. 9, ll. 2-4). The use of water in this embodiment is limited to precipitation and isolation of a *perphenysilane* (i.e. a silane substituted exclusively with phenyl groups; in this case, dodecaphenylcyclohexasilane) from the reaction medium.

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The crude dodecaphenylcyclohexasilane is then recrystallized from ethyl acetate (cf. Matsuki, col. 9, ll. 4-6), affording pure dodecaphenylcyclohexasilane, which is perchlorinated by sequential treatment with aluminum chloride in toluene, then hydrogen chloride gas, yielding dodecachlorocyclohexasilane (cf. Matsuki, col. 9, ll. 7-13). The crude mixture is then treated with lithium aluminum hydride (LAH) suspended in diethyl ether, and filtered to obtain a solution of silylcyclopentasilane in diethyl ether and toluene (cf. Matsuki, col. 9, ll. 14-19). Matsuki does not disclose isolating or purifying the desired silylcyclopentasilane.

Matsuki discloses a second method of preparing silylcyclopentasilane. Octaphenylcyclobutasilane is treated with lithium metal in dry, argon purged THF, then titrated with triphenylsilylphenyldichlorosilane (cf. Matsuki, col. 10, ll. 1-9). The reaction mixture is poured into ice water to precipitate the reaction product (cf. Matsuki, col. 10, ll. 10-11). The solution is subsequently filtered, washing the retained precipitate sequentially with water and cyclohexane, then drying under vacuum, yielding triphenylsilylnonaphenylcyclopentasilane (cf. Matsuki, col. 10, ll. 12-15). The use of water in this embodiment is again limited to precipitation and isolation of a perphenylsilane (in this case, triphenylsilylnonaphenylcyclopentasilane) from the reaction medium.

The product triphenylsilylnonaphenylcyclopentasilane is then perchlorinated and hydrogenated in a two-step process, by sequential treatment with aluminum chloride in toluene, then hydrogen chloride gas, then reduction of the resultant crude perchlorinated product with LAH in diethyl ether (cf. Matsuki, col. 10, ll. 15-23). The mixture is dried over silica gel then filtered and concentrated to obtain silylcyclopentasilane (cf. Matsuki, col. 10, ll. 23-25).

Matsuki further discloses a method of preparing a mixture of cyclopentasilane and silylcyclopentasilane. Treatment of diphenyldichlorosilane with metallic lithium in dry, argon purged THF affords an 8:1 mixture of major component decaphenylcyclopentasilane and by-product dodecaphenylcyclohexasilane (cf. Matsuki, col. 10, ll. 48-57). The crude product mixture is precipitated from the reaction medium by pouring into ice water (cf. Matsuki, col. 10, ll. 57-59). The use of water in this method is again limited to precipitation and isolation of

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perphenylsilanes (in this case, decaphenylcyclopentasilane and dodecaphenylcyclohexasilane) from the reaction medium.

Sequential perchlorination and hydrogenation as previously described furnishes an 8:1 mixture of cyclopentasilane and silylcyclopentasilane, respectively (cf. Matsuki, col. 11, ll. 7-19). Alternatively, recrystallization of the decaphenylcyclopentasilane/dodecaphenylcyclohexasilane mixture from ethyl acetate affords pure decaphenylcyclopentasilane (cf. Matsuki, col. 11, ll. 26-28), which is subjected to sequential perhalogenation and hydrogenation as described for the decaphenylcyclopentasilane/dodecaphenylcyclohexasilane mixture to obtain silylcyclopentasilane (cf. Matsuki, col. 11, ll. 28-31).

Matsuki then discloses a method of preparing a mixture of cyclopentasilane and spiro[4,4]nonasilane. Treatment of a mixture of diphenyldichlorosilane and tetrachlorosilane with lithium in dry, argon purged THF (cf. Matsuki, col. 12, ll. 10-20), isolation of the product mixture by quenching with ice water, followed by filtration and washing of the retained precipitate sequentially with water and cyclohexane affords a 9:1 mixture of major component decaphenylcyclopentasilane and by-product hexadecaphenylspiro[4,4]nonasilane (cf. Matsuki, col. 12, ll. 20-24). The use of water in this method is again limited to precipitation and isolation of perphenylcyclosilanes (in this case, decaphenylcyclopentasilane and hexadecaphenylspiro[4,4]nonasilane). Sequential perchlorination and hydrogenation as previously described affords a 9:1 mixture of cyclopentasilane and spiro[4,4]nonasilane (cf. Matsuki, col. 12, ll. 35-51).

Matsuki neither discloses nor suggests a method of preparing a hydrogenated Group IVA compound by washing a metal-contaminated perhydrosilane with a washing solution comprising deionized water. Each instance of the use of water in Matsuki as enumerated above effects the precipitation and isolation of perphenylsilanes, not a hydrogenated Group IVA compound as recited in Claim 1. Washing a metal-contaminated perhydrocyclosilane with a washing solution comprising deionized water to decontaminate the perhydrosilane is neither disclosed nor suggested by Matsuki. The washing recited in Claim 1, step (b) enables a significant reduction of the amount of metal contaminants present in the silane (cf. paragraph [0064], this application),

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resulting in a significant reduction of metal contamination in a corresponding Si film after spin coating (cf. paragraph [0065], present application).

Therefore, Matsuki does not disclose all of the limitations of Claim 1. As a result, the rejection of Claim 1 under 35 U.S.C. § 102(b) as being anticipated by Matsuki should be withdrawn. Claims 3-16, 18-28, 37, and 38 are dependent on Claim 1, and thus include all of the limits of Claim 1. Therefore Claims 3-16, 18-28, 37, and 38 are patentable over Matsuki for at least the same reasons as Claim 1.

With respect to Claim 74, Matsuki neither discloses nor suggests separating a washing composition containing metal contaminants from a hydrogenated Group IVA compound (cf. Claim 74, step (c)). Matsuki discloses a method of preparing a solution composition of cyclopentasilanes and/or silylcyclopentasilanes by dissolving one or more of the compound(s) in an appropriate solvent (cf. Matsuki, col. 5, ll. 35-37). Preferred examples of solvents include hydrocarbon-based solvents such as n-heptane, n-octane, decane, toluene, xylene, cymene, durene, indene, dipentene, tetrahydronaphthalene, decahydronaphthalene, and cyclohexylbenzene; ether-based solvents such as ethylene glycol dimethyl ether, ethylene glycol diethyl ether, ethylene glycol methyl ethyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol methyl ethyl ether, and p-dioxane; and aprotic solvents such as propylene carbonate, γ -butyrolactone, N-methyl-2-pyrrolidinone, dimethylformamide, dimethylsulfoxide and cyclohexanone (cf. Matsuki, col. 5, ll. 39-49). Matsuki further discloses the solubility of silylcyclopentasilane in hydrocarbon-based solvents, exemplified by benzene, toluene, xylene, hexane, cyclohexane, indane and decahydronaphthalene; ether-based solvents exemplified by diethyl ether, tetrahydrofuran, monoglyme and diglyme; or ketone based solvents exemplified by acetone, methyl ethyl ketone, methyl isobutyl ketone or methyl amyl ketone (cf. Matsuki col. 9, ll. 39-45).

Matsuki discloses these solvents and the solubility of cyclopentasilanes therein for the express purpose of preparing solution compositions of silylcyclopentasilanes to form a coating film of the solution composition (cf. Matsuki, col. 6, ll. 18-19). To the extent that Matsuki combines a solvent with a perhydrosilane, it does not appear that the solvent is immiscible,

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otherwise Matsuki could not form a solution composition as taught. However, assuming one or more of the solvents disclosed by Matsuki is immiscible with a perhydrosilane (presuming for the sake of argument that it contains metal contaminants), the immiscible solvent is not separated from the perhydrosilane. The solvent is removed from the described solution composition by vaporization (heating after application to form a coating film; cf. Matsuki, col. 6, ll. 42-44), which one of ordinary skill in the art would expect to leave in the deposited film any metal contaminants that might have been in the solvent. Thus, Matsuki neither discloses nor suggests separating a washing composition containing metal contaminants from a hydrogenated Group IVA compound as recited in Claim 74, step (c).

Therefore, Claim 74 is patentable over Matsuki. Claims 75-111 are dependent on Claim 74 and thus include all the limitations of Claim 74. Therefore Claims 75-111 are patentable over Matsuki for at least the same reasons as Claim 74.

The Rejection of Claims 1, 3-16, 18-28, 37 and 38 under 35 U.S.C. § 103(a)

The rejection of Claims 1, 3-16, 18-28, 37, and 38 under 35 U.S.C. § 103(a) as being obvious over Matsuki is respectfully traversed. As stated above, Matsuki does not disclose or suggest a method of making a hydrogenated Group IVA compound, including washing a metal-contaminated, hydrogenated Group IVA compound with a washing composition comprising deionized water to decontaminate the metal-contaminated, hydrogenated Group IVA compound (Claim 1, step (b)), nor does Matsuki disclose or suggest separating a washing composition comprising a polar immiscible solvent containing metal contaminants from the hydrogenated Group IVA compound (Claim 74, step (c)).

The reactivity of Si-H bonds is well known (cf. Cotton, F. A. et al., Advanced Inorganic Chemistry, 6th Ed.; New York, John Wiley & Sons, inc., 1999, p. 268-270; submitted herewith; hereinafter, "Cotton"). Under basic conditions, hydrosilanes are hydrolytically unstable (cf. Cotton, p. 269). One could reasonably expect the product mixture from the reduction of a perchlorosilane (e.g. Matsuki, col. 10, ll. 36-40) to contain a number of species that are

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potentially reactive with water, that could give rise to species (e.g. basic species) that would have hydrolytic reactivity toward Si-H bonds. For example, lithium aluminum hydride is known to react rapidly with protic solvents (e.g., water), liberating molecular hydrogen, yielding alane (AlH_3) and the corresponding alkoxide of the protic solvent used (e.g., for water, hydroxide anion; cf. Carey, F. A. and Sundberg, R. J., Advanced Organic Chemistry, Part B: Reactions and Synthesis, 4th Ed.; New York, Kluwer Academic/Plenum Publishers, 2001, p. 265; submitted herewith). Therefore, one could reasonably expect washing such a product mixture with water could potentially lead to a number of undesired side reactions, including decomposition (e.g., hydrolysis) of the perhydrosilane. Thus, prior to the present invention, the method of Claim 1 would not have been obvious to one of ordinary skill in the art.

As a result, the rejection of Claim 1 under U.S.C. § 103(a) as being obvious over Matsuki should be withdrawn. Claims 3-16, 18-28, 37, and 38 depend directly or indirectly from Claim 1, and thus include all of the limits of Claim 1. Therefore Claims 3-16, 18-28, 37, and 38 are patentable over Matsuki for at least the same reasons as Claim 1.

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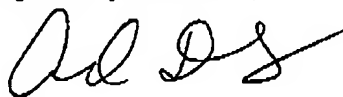
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Conclusions

In view of the above amendments and remarks, all bases for rejection are overcome, and the application is in condition for allowance. Early notice to that effect is earnestly requested.

If it is deemed helpful or beneficial to the efficient prosecution of the present application, the Examiner is invited to contact Applicant's undersigned representative by telephone.

Respectfully submitted,



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Reg. No. 34,600

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268 chapter 8/THE GROUP 14 ELEMENTS: Si, Ge, Sn, Pb

Table 8-4 Tetraivalent Hydrides and Halides of Group 14 Elements

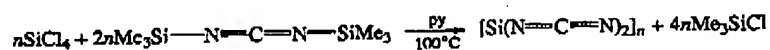
Hydrides ^a		Fluorides and Chlorides ^b		
MH ₄	Other	MF ₄	MCl ₄	Other
SiH ₄ bp -112°C	Si ₂ H ₆ → Si ₆ H ₁₄ bp -145°C	SiF ₄ subl -95.7°C	SiCl ₄ bp 57.6°C mp -70°C	Si ₂ Cl ₆ → Si ₄ Cl ₁₄ bp -145°C Si ₂ F ₆ → Si ₁₀ F ₃₄ bp -18.5°C Si ₂ Br ₆ mp 90.8°C Ge ₂ Cl ₆ mp 40°C Ge ₃ F ₁₂ Ge + GeF ₄ → Ge ₇ F ₁₆ ^c
GeH ₄ bp -88°C	Ge ₂ H ₆ → Ge ₃ H ₂₀ bp -29°C	GeF ₄ subl -37°C	GeCl ₄ bp 83°C mp -49.5°C	
SnH ₄ bp -52.5°C PbH ₄ (?)	Sn ₂ H ₆	SnF ₄ subl 704°C PbF ₄	SnCl ₄ bp 114.1°C PbCl ₄ d. 105°C	

^aThere are mixed Si-Ge hydrides and cyclo silanes as well as isomers that may be separable by g.l.c.

^bAll MX₄ compounds except PbBr₄ and PbI₄ are known, as well as mixed halides of Si (e.g., SiF₃I and SiFCl₂Br) and even SiFClBrI.

^cJ. Köhler and J.-H. Chang, *Z. anorg. allg. Chem.* 1997, 623, 596.

Finally, ceramic composites belonging to the ternary Si-C-N system are of high technical relevance. Crystalline solids of composition SiC₂N₄²⁸ have a polymeric network structure; they are made according to:



THE TETRAVALENT STATE

8-5 Hydrides

All the hydrides, Table 8-4, are colorless.

Silanes

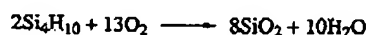
Monosilane (SiH₄) is best prepared on a small scale by heating SiO₂ and LiAlH₄ at 150 to 170°C. On a larger scale SiO₂ or alkali silicates are reduced by a NaCl-AlCl₃ eutectic (mp 120°C) containing Al metal, or with hydrogen at 400 atm and 175°C. The original Stock procedure of acid hydrolysis of magnesium silicide gives a mixture of silanes. Chlorosilanes may also be reduced by LiAlH₄. Higher silanes can also be made by photolysis of SiH₄-H₂ mixtures.

Only SiH₄ and Si₂H₆ are indefinitely stable at 25°C; the higher silanes decompose giving H₂ and mono- and disilane, possibly indicating SiH₂ as an intermediate.

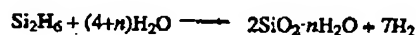
²⁸R. Riedel *et al.*, *Angew. Chem. Int. Ed. Engl.* 1997, 36, 603.

8-5 Hydrides 269

The hydridic reactivity of the Si—H bond in silanes and substituted silanes may be attributed to charge separation $\text{Si}^{\delta+}-\text{H}^{\delta-}$ that results from the greater electronegativity of H than of Si. Silanes are spontaneously flammable in air, for example,

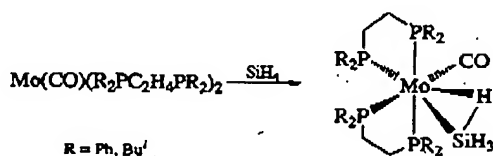


Although silanes are stable to water and dilute mineral acids, rapid hydrolysis occurs with bases;

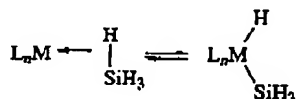


The silanes are strong reducing agents. With halogens they react explosively at 25°C, but controlled replacement of H by Cl or Br may be effected in the presence of AlX_3 to give halogenosilanes such as SiH_3Cl .

Transition metal complexes in which SiH_4 is coordinated in a η^2 -fashion *via* a Si—H σ bond have been prepared according to



Those compounds show a tautomeric equilibrium between the η^2 - SiH_4 complex and the hydrosilyl species:²⁶



Monogermane together with Ge_2H_6 and Ge_3H_8 can be made by heating GeO_2 and LiAlH_4 or by addition of NaBH_4 to GeO_2 in acid solution. Higher germanes are made by electric discharge in GeH_4 . Germanes are less flammable than silanes, although still rapidly oxidized in air, and the higher germanes increasingly so. The reaction of GeH_4 with ozone in solid argon produces a variety of species such as the transient germanone (H_2GeO), a germylene-water complex ($\text{H}_2\text{O}-\text{GeH}_2$), hydroxygermylene, germanic acid, and germanol.²⁷ However, the germanes are resistant to hydrolysis, and GeH_4 is unaffected by even 30% NaOH .

Stannane (SnH_4) is obtained by interaction of SnCl_4 and LiAlH_4 in ether at -30°C . It decomposes rapidly when heated and yields β -tin at 0°C . Although it is stable to dilute acids and bases, 2.5 M NaOH causes decomposition to Sn and some stannate. Stannane is easily oxidized and can be used to reduce organic compounds (e.g., $\text{C}_6\text{H}_5\text{CHO}$ to $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$, and $\text{C}_6\text{H}_5\text{NO}_2$ to $\text{C}_6\text{H}_5\text{NH}_2$). With concentrated

²⁶X. L. Luo *et al.*, *J. Am. Chem. Soc.* 1995, 117, 1159.

²⁷R. Withnall and L. Andrews, *J. Phys. Chem.* 1990, 94, 2351.

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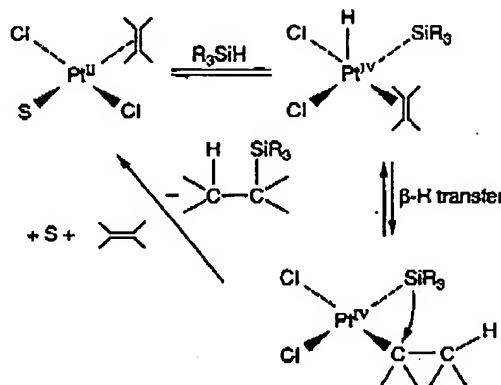
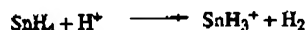


Figure 8-2 Simplified cycle for hydrosilation of alkenes by platinum complexes (S = solvent).

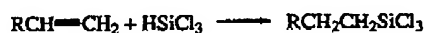
acids at low temperatures, the solvated stannonium ion is formed by the reaction



Plumbane (PbH_4) is said to be formed in traces when Mg–Pb alloys are hydrolyzed by acid or when Pb^{2+} salts are reduced cathodically, but its existence is doubtful.²⁸

All the elements form stable organohydrides ($\text{R}_n\text{MH}_{4-n}$); they are readily made by reduction of the corresponding chlorides with LiAlH_4 . There are also a number of compounds of transition metals with silyl groups [e.g., $\text{H}_3\text{SiCo}(\text{CO})_4$].

Perhaps the most important reaction of compounds with an Si–H bond, such as Cl_3SiH or Me_3SiH , and one that is of commercial importance, is the Speier or hydrosilation²⁹ reaction of alkenes, for example:



Olefins usually give the terminal product. The reaction is catalyzed by transition metal complexes, e.g., H_2PtCl_6 or $\text{RhCl}(\text{PPh}_3)_3$; it may involve the oxidative addition of Si–H bonds across a transition metal as shown in Fig. 8-2.

Silicon tetrahydride and GeH_4 react with K, Rb, and Cs to form H_3SiM^+ and H_3GeM^+ , which have NaCl type structures at room temperature; more complex structures are known for other cations.³⁰

The unusual reducing properties of SiHCl_3 are discussed in Section 8-6.

8-6 Halides

The more important halides are given in Table 8-4.

²⁸See for example: W. Thiel *et al.*, *J. Phys. Chem.* **1993**, *97*, 4381 and references therein.

²⁹M. Brookhart and B. E. Grant, *J. Am. Chem. Soc.* **1993**, *115*, 2151; A. R. Cutler *et al.*, *J. Am. Chem. Soc.* **1995**, *117*, 10139.

³⁰W. Sundermeyer *et al.*, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 216.

Advanced Organic Chemistry

FOURTH
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Part B: Reactions and Synthesis

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Preface

The front cover shows the key orbital interactions in the Diels-Alder reaction. The highest-occupied molecular orbital (HOMO) of 1,3-butadiene and the lowest-unoccupied molecular orbital (LUMO) of ethylene overlap in phase with one another allowing the reaction to occur in a single step.

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Part B emphasizes reactions organized by re carbonyl addition. Chapter 3 covers carbonyl group additions to all reactions, emphasizing especially Diels-Alder reactions considered in intermediates: zinc are covered palladium, and and stannanes. tions, carbene: electrophilic and most important chapters, the role of typical processes the use of processes with several: epothilone. The application in torial synthesis

The content of organic chemistry advances have catalytic processes scope and efficiency optimization and are catalysts for

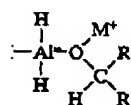
Agents

	Carboxy- late salt
Amide	
Amine	Alcohol
Amine	Alcohol
Aldehyde ^a	
Amine	Alcohol ^a
Amine	Alcohol
Aldehyde ^a	
Aldehyde ^a	Alcohol

reaction has not been studied

ad B. C. Sabba Rao, *J. Am.*S. Park, H. C. Brown, *S. g. Chem.* 38:912 (1973)J. Brown and V. Varma, *J. Res.* 4:47 (1969); N. M.

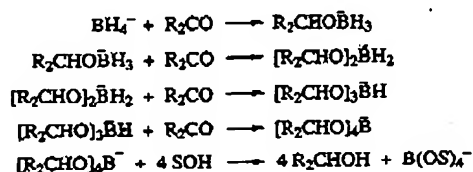
involves nucleophilic attack of the carbonyl group by hydride ions. As reduction proceeds, aluminum can



re actually several
 Although this
 does not detract from
 lone in aqueous or

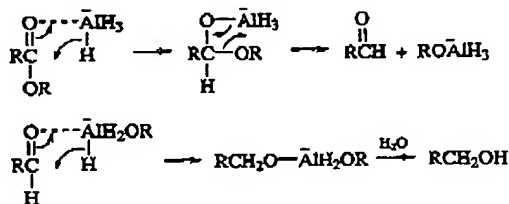
alcoholic solution, and the alkoxyboranes formed as intermediates are rapidly solvolyzed.

265

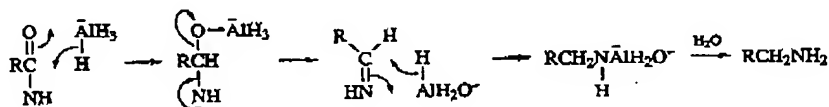
SECTION 5.2.
GROUP III HYDRIDE
DONOR REAGENTS

The mechanism for reduction by LiAlH_4 is very similar. However, because LiAlH_4 reacts very rapidly with protic solvents to form molecular hydrogen, reductions with this reagent must be carried out in aprotic solvents, usually ether or THF. The products are liberated by hydrolysis of the aluminum alkoxide at the end of the reaction.

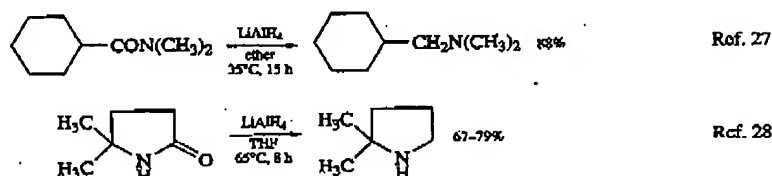
Hydride reduction of esters to alcohols involves elimination steps, in addition to hydride transfer.



Amides are reduced to amines because the nitrogen is a poorer leaving group than oxygen at the intermediate stage of the reduction. Primary and secondary amides are rapidly deprotonated by the strongly basic LiAlH_4 , so the addition step involves the conjugate base.



Reduction of amides by LiAlH_4 is an important method for synthesis of amines:



Several factors affect the reactivity of the boron and aluminum hydrides. These include the metal cation present and the ligands, in addition to hydride, in the metallo

27. A. C. Cope and E. Ciganek, *Org. Synth.* IV:339 (1963).28. R. B. Moffett, *Org. Synth.* IV:354 (1963).